

Evaluation of cationic polymers to control pitch deposition

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SUMMARY

A wide range of cationic polymers of varying chemical structure, charge density and molar mass were evaluated for their effectiveness to control wood resin deposition. The ability of the polymers to attach model wood resin particles to thermo-mechanical pulp fibres and to maintain the wood resin in the colloidal phase was determined at pH 4.75, 6.85 and 8.06.

High molar mass poly-DADMAC, copolymer poly-(AM-co-DADMAC) and guar gum were found to be the best fixatives over the pH range investigated. The performance of poly-DADMAC was found to increase with molar mass and charge density.

A conceptual model was proposed to explain the behaviour of the polymers based on their ability to stabilise the wood resin colloids, to attach the wood resins to pulp fibres and to affect the wood resin particle size.

KEYWORDS

wood resins, pitch deposition, fixatives, cationic polymers

INTRODUCTION

The deposition of wood pitch has been a problem for the pulp and paper industry for many years. Many approaches have been used to reduce the problem. The use of water soluble cationic polymers (often called fixatives) has been a popular choice for many pulp and paper manufacturers in controlling pitch in the wet-end of the paper machine. The main reasons for their popularity are the low capital cost, the fact that there is a wide array to choose from, and also that switching from one to

another is a simple matter. They have been also found to be more effective than talc and alum (1).

The range of synthetic water soluble polymers that have been used for pitch control include polyamines, poly(diallyldimethylammonium chloride) (pDADMAC) (2-5), cationically modified polyacrylamide (cPAM) (6,7,8), polyvinylamines (pVAm) (5,9), polyethylenimines (pEI) (4,5,7-11), and more recently co-polymers of acrylamide and diallyldimethylammonium chloride (p(AM-co-DADMAC) (7,10,12).

Due to the large number of process variables within the pulp and paper process, selecting a specific fixative, and knowing when the process has changed to such an extent that a different fixative chemistry is required, is a daunting task. There are a number of studies evaluating fixatives though most compare only 2 or 3 different types of fixatives (1,7-10,13).

Several mechanisms have been proposed to explain how cationic polymers work as fixatives. It is believed that they are adsorbed onto anionic pitch particles, stabilising the pitch particles and so preventing aggregation that may lead to deposition. They are also believed to attach the dispersed pitch particles onto the fibres. Another possible mechanism is that they agglomerate the pitch particles which then become entrapped in the fibre web (2,14)

A study (15) was undertaken recently investigating the effect of a range of cationic polymers on the colloidal stability of wood resin dispersions under varying pH conditions. The study showed that fixatives could be divided into two categories, colloid disrupting and colloid stabilizing, according to how they changed wood resin particle size. This paper builds on that study and investigates the same range of polymers as to their effect on

1. the deposition tendency or fixation of wood resins onto the fibre surface and
2. the stabilisation of the wood resin colloids in the colloidal phase in the papermaking system.

The aim of the study was to better understand the mechanisms by which dif-

ferent fixatives are able to interact with wood resin colloids and pulp fibres.

EXPERIMENTAL

Pulp

Thermomechanical pulp (TMP) of *Pinus radiata* was collected from the primary refiners at the Norske Skog Boyer mill in Tasmania. The pulp was air dried and then Soxhlet extracted with hexane to remove extractives. The pulp was kept in the freezer at -4°C until ready for use. The fibres were rehydrated to 1% consistency by adding 4g oven dry fibre to the wood resin colloidal solutions.

Wood Resin Colloidal Dispersions

Model wood resin colloidal dispersions were prepared using a variation on methods developed by both Sundberg *et al* (16) and Stack *et al* (17). The model dispersions were made by mixing acetone (99.5% purity) solutions of a fatty acid (oleic acid, 99+% purity), a triglyceride (triolein, 99% purity) and a resin acid (abietic acid, 70% purity technical grade) in distilled water containing 1mM KNO₃ and that had been pH adjusted to 5.5. This dispersion was dialysed for 24 hours to remove the acetone. The concentrations of wood extractive components were 40 mg/L abietic acid, 40 mg/L oleic acid and 55 mg/L triolein after dialysis.

Buffers

Three 20mM amine buffers were used to control the pH. Tris(hydroxymethyl)aminomethane (pK_a 8.06) and ethylenediamine (pK_a 6.85) were obtained from Aldrich and prepared in distilled water. N,O-dimethylhydroxylamine was obtained by distilling (at 100°C) the hydrochloride salt with a molar excess of KOH to obtain the free amine with a yield of 82.5%. Each buffer solution was titrated with 1M HCl until the pH of the buffer equalled the pK_a of the amine.

Cationic polymers

Fifteen different cationic polymers were obtained from Norske Skog Boyer who

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received them for evaluation from various suppliers. These were labelled as FixA through to FixO. The information obtained for each fixative investigated is presented in Table 1. The viscosity average molar mass of the polymers was determined from viscosity measurements of the polymers using an Ubbelohde viscometer and the Mark-Houwink equation (18). The Mark-Houwink constants were obtained from the literature (19).

The charge densities of the fixatives were determined by titration of 10mL of a 1% solution of fixative as supplied with 0.001N sodium polyethylene sulphate (PES-Na) using a Mutek PCD-02 (Particle Charge Detector) to determine the charge neutralisation endpoint.

The % solids were determined by drying a sample at 60°C for 48 hours.

Deposition (fixation) tendency

Fixation tendency of the polymers was determined by measuring how well the polymers deposited (fixed) the wood resins onto the fibre surface. These deposition experiments were conducted using a similar method to that of Maher *et al* (7). 400 mL of the model wood resin solutions were added to glass jars. 1 mL of 0.5M pH buffer was added to each jar followed by 4g of soxhlet extracted air dried TMP fibres. 1.6 mL of 0.5% fixative was added to the jar. This dosage was equivalent to 2 kg of 'as received' fixative per oven dried tonne of TMP. The jars were stirred at a constant rate of 330 rpm using paddle stirrers (Cole Palmer, PE coated) for a period of 30 minutes in a 50°C temperature bath.

Wood Resin Analysis

The model wood resin components were extracted from the dispersions, using tertiary butyl methyl ether (*t*-BME). They were then silylated and the fatty acid (FA), resin acid (RA) and triglyceride (TG) concentration analysed by gas chromatography (GC) analysis as described previously (20).

The total concentration of wood resins at the start prior to stirring and at the end of stirring was measured. The difference between the two results represented the amount of surface bound material. The distribution of the wood resins between the fibre bound fraction, colloidal fraction, and soluble fraction after deposition was also determined. The dissolved and colloidal fraction (DCS) was obtained by centrifug-

Table 1
Physical properties of Cationic Polymers

Label	Chemistry	% Solids	Molar Mass*	Viscosity Av Molar mass
FixA	pDADMAC	43	Low	2.0×10^3
FixB	pDADMAC	39	Medium	1.5×10^4
FixC	pDADMAC	21	Medium	2.3×10^4
FixD	cPAM	58	High	1.3×10^7
FixE	cPAM	45	High	6.0×10^7
FixF	cPAM	58	High	5.9×10^7
FixG	Guar gum	100		
FixH	p(AM-co-DADMAC)	67	Medium	
FixI	p(AM-co-DADMAC)	63	Medium	
FixJ	pAC	47	Low	
FixK	Epi-DMA	52	Medium	3.4×10^5
FixL	PEI	26	Low	6.0×10^3
FixM	PEI	28	Low	
FixN	pVAm	35	Low	1.8×10^3
FixO	pVAm	17	Medium	1.0×10^5

* Low MW= $<10^4$, Medium MW= 10^4 - 10^6 , High MW= $>10^7$

ing a sample of the total solution for 10 minutes at 1800 rpm (500G). The soluble fraction was obtained by filtering part of the DCS fraction through a 0.1 micron filter and collecting the filtrate. All samples were extracted using *t*-BME. The amount of fibre bound extractives (i.e. fixed pitch) was determined from the difference between the total concentration after deposition and the DCS concentration. The amount in the colloidal fraction was determined from the difference between the DCS and the soluble fractions.

RESULTS

Polymer Charge density

The charge densities in meq/g o.d. of each of the fifteen cationic polymers were determined at the three pH levels examined (Figure 1). The pEI group (Fix L and Fix

M) were found to have the highest charge density of the polymers studied at pH 4.75, with Fix L being lower in charge density compared to Fix M. The charge density of both Fix L and M were found to vary with pH. This is because the charged groups in pEI are a combination of primary, secondary, and tertiary ammonium cations.

Other cationic polymers such as pDADMAC (Fix A, Fix B and Fix C), which make use of quaternary ammonium cations, should be independent of the pH, but some variation in charge density of Fix B and Fix C were found with changes in pH. This may be associated with the formation of quaternary ammonium cations by surrounding a nitrogen centre with four alkyl groups – a process which is not always carried out to 100% completion – and thus the cationic charge of the non-quaternised nitrogen centres

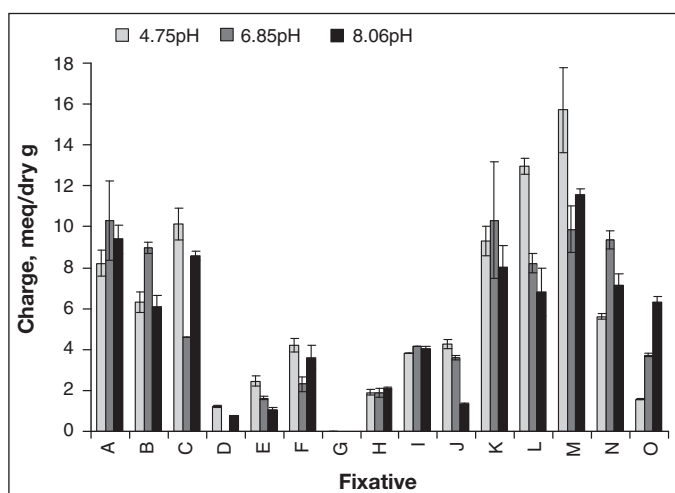


Fig. 1 Cationic charge density in meq / dry gram of cationic polymers (Error bars are the range of replicates).

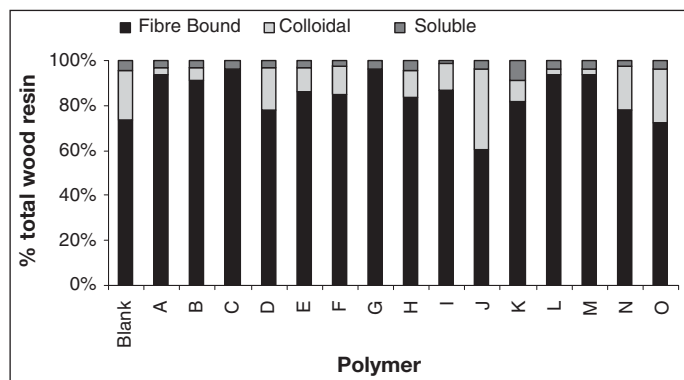


Fig. 2 Comparison of cationic polymers performance for fixation of wood resins onto fibres at 4.75pH and 2kg/tonne polymer addition.

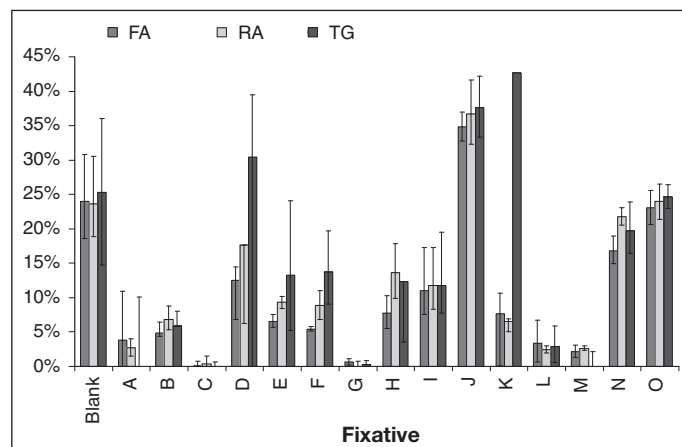


Fig. 3 Effect of cationic polymers on the % extractive components in the colloidal phase after deposition at 4.75pH (FA=fatty acid, RA=resin acid, TG=triglyceride).

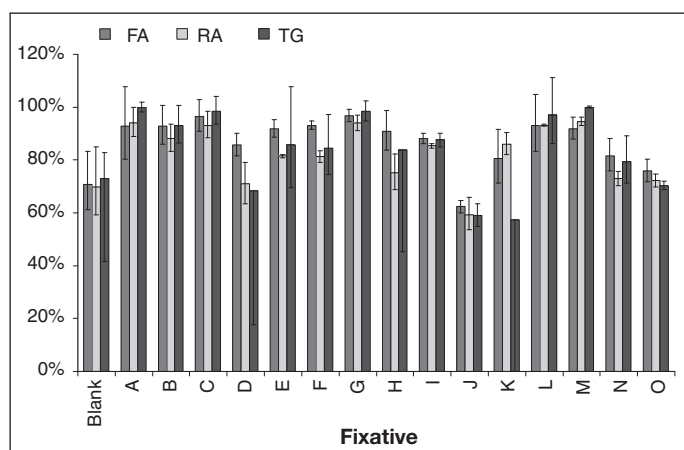


Fig. 4 Effect of cationic polymers on the % extractive components fixed to the fibres after deposition at 4.75pH (FA=fatty acid, RA=resin acid, TG=triglyceride).

decreases as pH increases. It is also possible that cationic impurities may be present or the polymers have been modified in undisclosed ways by the manufacturer.

The cPAM group (Fix D, Fix E and Fix F) and the copolymers p(AM-co-DADMAC) (Fix H and Fix I) were found to have low charge density while guar gum (Fix G) was found to have no cationic charge. Within the group of three cPAMs studied, the charge density of the polymers increased from Fix D through to Fix F. Similarly the charge density of the two copolymers increased with Fix I being higher charge density than Fix H.

Unlike the other polymers in which the charge density was found to decrease, or remain unchanged with increasing pH, Fix O (pVAm) showed increased charge density with increasing pH. It is possible that Fix O was modified with other functionalities by the manufacturers. Another reason for this behaviour could be that Fix O was so tightly coiled (i.e. near crystalline), as received, that it did not sufficiently uncoil until exposed to higher pH solvents.

Fixation of wood resins at pH 4.75

Figure 2 compares how the various polymers affect the distribution of total wood resin extractives between the fibre bound, colloidal and dissolved fractions at pH 4.75 (at an addition of 2 kg/tonne after 30 minutes of stirring at 50°C). At this pH and in the absence of cationic polymers (i.e. the blank), 75% of the extractives were found to attach to the fibres while 20% were found as colloids in the liquid phase and 5% were dissolved (i.e. $< 0.1 \mu\text{m}$).

Figure 2 shows that the addition of the pDADMACs (Fix A, Fix B and Fix C), Guar Gum (Fix G) and pEI (Fix L and Fix M) increased the amount of wood resin bound to the fibres and decreased the amount in the colloidal phase. These polymers, at pH 4.75, would thus be considered good “fixatives”. The better performance of these polymers is not strictly related to charge density because although PEI and pDADMAC have the higher charge densities at pH 4.75, Guar Gum has no cationic charge. These pDADMAC and pEI polymers tend to be low to medium molar mass.

A smaller increase in fibre bound wood resin was observed with the addition of cPAM (Fix D, Fix E and Fix F), copolymers p(AM-co-DADMAC) (Fix H and Fix I), Epi-DMA (Fix K) and Fix N (pVAm). Fix J (pAC) and Fix O (pVAm) were found to either have no effect or to decrease the amount of wood resin bound to the fibres. An increase in the amount of wood resin in the colloidal phase was found to occur. This would cause accumulation of extractives in the white water loop of paper-machines if they operated at this pH.

There are no clear trends in the effect of charge density between the different polymers. Increasing the charge density of pVAm (FixN and Fix O) and the copolymer (Fix I and Fix H) seems to result in better fixation. No trend was observed for the pEIs, cPAMs and pDADMACs.

The effects of the cationic polymers on the distribution of each of the three components (fatty acid (FA), resin acid (RA) and triglyceride (TG)) in the wood resin in the colloidal phase and on the fibres are shown in Figures 3 and 4. FixK (Epi-DMA) and pAMs (FixD, FixE and FixF), to a lesser extent, appear to cause more of the triglyceride to be retained in the colloidal phase and less on the fibres.

Fixation of wood resins at pH 6.85

At pH 6.85, the wood resin distribution is slightly different than at pH 4.75. The blank showed a higher amount of the wood resin was bound to the fibres and slightly less in the colloidal phase. The results (Fig. 5) show that only some of the polymers achieved better fixation at pH 6.85 compared to 4.75. Fixative D and the copolymers (Fix H and Fix I) were found to be the best polymers for fixation at pH

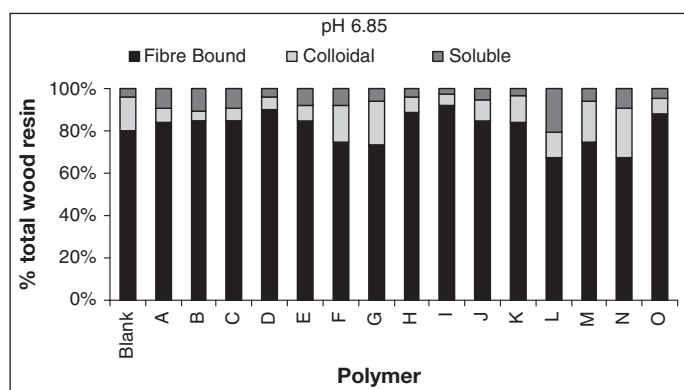


Fig. 5 Comparison of cationic polymers performance for fixation of wood resins at 6.85 pH and 2 kg/tonne polymer addition.

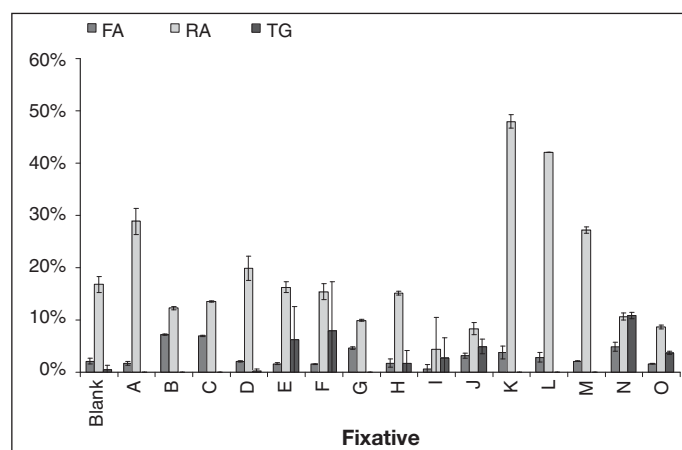


Fig. 6 Percent of the extractive components in the dissolved (i.e. <0.1 µm) phase after deposition at 6.85 pH (FA=fatty acid, RA=resin acid, TG=triglyceride).

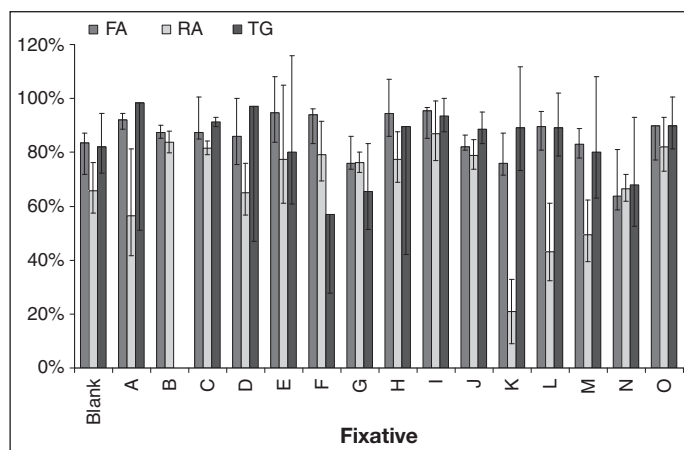


Fig. 7 Percent of the extractive components fixed to the fibres after deposition at 6.85pH (FA=fatty acid, RA=resin acid, TG=triglyceride).

6.85 and performed better than at pH 4.75. The pDADMACs (Fix A, Fix B and Fix C) achieved a slight increase in fibre fixation compared to the blank but achieved lower fixation than at pH 4.75. These three fixatives did reduce the amount of material in the colloidal phase. The fixation of wood resins by cPAM was higher than the blank for Fix D and Fix E with a corresponding reduction in the amount in the colloidal phase but this result is lower than at pH 4.75. The addition of Fix F (cPAM) resulted in a decrease in the amount of wood resin bound to the fibres and a slight increase in the amount in the colloidal phase and in the soluble phase. Fix F had a similar molar mass but higher charge density than Fix E (cPAM).

FixG (Guar gum), FixM (pEI) and FixN (pVAm) were all found to increase the amount of wood resin in the colloidal phase and reduce the amount fibre bound, indicating these polymers may have a stronger interaction with the wood resins and act to stabilise the wood resin colloids more than fixing them to the fibres.

pEI (FixL & FixM) showed lower fixation at pH 6.85 than at 4.75. This result is expected given that its cationic charge decreases with increased pH (21). FixL (pEI) was shown to displace twice the amount of extractive material into the dissolved phase (i.e. <0.1 µm) than the other fixatives. This may be a result of an interaction between pEI and the wood resin that forms soluble complexes with the dissociated soluble resin acids and fatty acids or small stabilised particles which are less than 0.1 µm and so pass through the filter paper and are classified as dissolved material.

When comparing the effect of the polymers on the different components in the wood resin, it can be observed (Fig. 6) that a large proportion of the dissolved (i.e. <0.1 µm) materials are resin acids and this is expected because the pH (6.85) is close to the pK_a of the resin acids (22). With some fixatives - notably, FixA (pDADMAC), FixK (Epi-DMA), and the pEI fixatives (FixL & FixM) - higher percentages of resin acids are present in the dissolved (i.e. <0.1 µm) phase.

Interestingly these fixatives have the highest cationic charge at pH 6.85, although FixB (pDADMAC) and FixN (pVAm) both have equally high cationic charge but do not displace the same high proportions of resin acids to the dissolved (i.e. <0.1 µm) phase.

As a result of the formation of soluble complexes between the polymers and the resin acids and/or the stabilisation of very small particles of resin acid (<0.1 µm) by FixA (pDADMAC), FixK (Epi-DMA) and the pEI fixatives (FixL & FixM) lower amounts of resin acids were found fixed to the fibres compared to the other polymers (Fig. 7).

Fixation of wood resins at pH 8.06

At pH 8.06, an increase in the amount of the wood resin in the colloidal phase and soluble phase compared to both pH 4.75 and pH 6.85 was observed in the blank (Fig. 8). At this pH, a large proportion of the resin acids and fatty acids would be in a soluble form as the pH is well above the pK_a for resin acids and close to the colloidal pK_a for oleic acid (22). As a result both the soluble resin acids and fatty acids would readily form complexes with the dissolved organic material released from the pulp fibres.

In all cases, except Fix J and Fix O, the fixatives were found to reduce the amount of colloidal material compared to the blank and to increase the fixation to the fibres, suggesting that the colloidal material was easily destabilised at pH 8.06. FixC (pDADMAC) and FixG (guar gum) were found to be the best fixatives at pH 8.06 and reduced the amount of colloidal material to very low levels.

At pH 8.06 clearer trends with molar

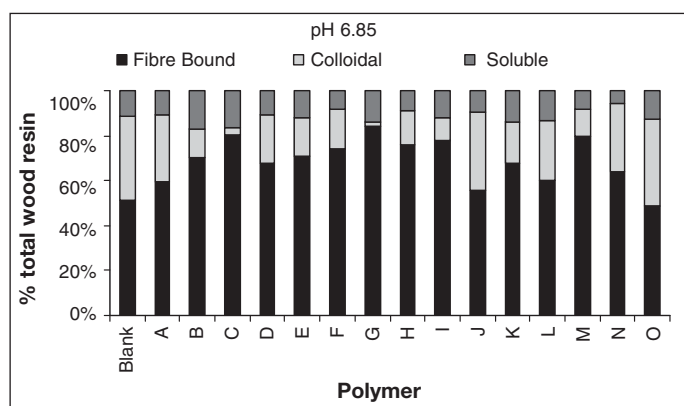


Fig. 8 Comparison of cationic polymers performance for fixation of wood resins onto fibres at 8.06 pH and 2kg/tonne polymer addition.

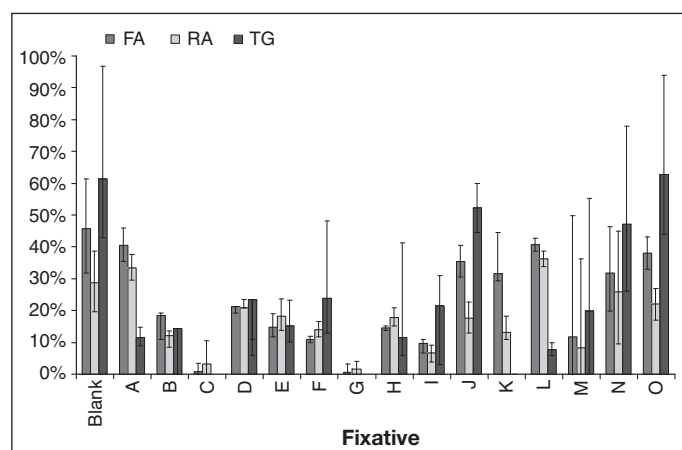


Fig. 9 Percent of the extractive components in the colloidal phase after deposition at 8.06 pH (FA=fatty acid, RA=resin acid, TG=triglyceride).

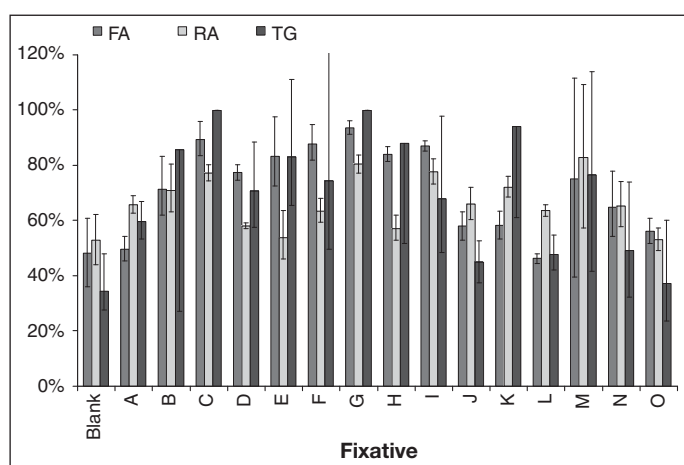


Fig. 10 Percent of the extractive components fixed to the fibre after deposition at 8.06 pH (FA=fatty acid, RA=resin acid, TG=triglyceride).

mass and charge density were observed. With increasing molar mass of pDADMAC (FixA, FixB, & FixC) less colloidal material in suspension and more fixation to fibres were found. pAM fixation ability at pH 8.06 is also found to be directly proportional to its molar mass as shown by examining FixD, FixE and FixF. The higher charged, lower molar mass, pEI (FixM) was found to fix more extractive material than its lower charged, higher molar mass alternative (FixL). The same relationship between charge, molar mass and the level of fixation was found with pVAm (FixN & FixO).

pDADMAC (Fix A, Fix B and Fix C) along with Fix K (Epi-DMA) and Fix L (pEI) were all found to preferentially reduce the amount of triglycerides in the colloidal phase (Fig. 9) and increase its fixation onto the fibres (Fig. 10) at pH 8.06.

DISCUSSION

It has been previously shown (7) that the model wood resin dispersions that were

prepared were stabilised by dissolved organic material released from the fibers in the same way the wood resins in the papermaking process are. Although the model wood resins only contain the three major components found in the wood resins extracted from *Pinus Radiata* it does provide a good model for the current investigation.

Table 3

Fixative categories as determined by colloidal fractions in 'as received' deposition studies.

pH	High colloidal fractions	Low colloidal fractions
4.75	FixJ, FixD, FixO	FixC, FixG, FixA, FixB, FixL, FixM
6.85	FixF, FixG, FixM, FixN	FixB, FixC, FixD, FixI
8.06	FixO, FixN, Fix J	FixC, FixG, FixI

Table 4

Fixative categories as determined by fixation in 'as received' deposition studies.

pH	Low fixation	High fixation
4.75	FixD, FixJ, FixO, FixN	FixC, FixG, FixA, FixB, FixL, FixM
6.85	FixF, FixG, FixL, FixM, FixN	FixD, FixH, FixI, FixO
8.06	FixJ, FixL, FixO, FixA, FixN	FixC, FixG, FixM

Table 5
Fixative categories as determined by Laser Particle Size Analyser (LPSA) (15).

pH	Colloid disrupting fixatives	Colloid stabilising fixatives
4.75	FixD, FixE Maybe: FixF, FixI, FixL, FixM	FixC, FixH, FixK, FixN, FixO, Maybe: FixJ, FixA, FixB
6.85	FixD, FixE, FixH Maybe: FixA, FixF, FixK	FixB, FixC, FixL, FixO, FixG Maybe: FixJ, FixM, FixN
8.06	FixA, FixB, FixD, FixE, FixH, FixK	FixC, FixJ, FixG Maybe FixF, FixI, FixL, FixM, Fix N, Fix O

colloidal particles to the fibres, aggregate and attach large particles, or aggregate particles that are not strongly adsorbed but entrapped in the fibre mat.

From the results in Tables 3 and 5, it can be seen that some of the polymers that are classed as “Colloid Stabilising” fixatives because they do not aggregate the wood resin particles - such as pVAm (Fix N and Fix O) and pAC (Fix J) - can result in higher amounts of material in the colloidal phase and low fixation to the fibres. This suggests that these polymers have a strong affinity with the wood resin and a lower affinity for the fibres and they stabilise the wood resin particles as small colloidal particles. Other polymers which are also classified as “Colloid Stabilising” such as Fix C (high MW pDADMAC) and guar gum

(Fix G) are shown to reduce the amount of material in the colloidal phase and attach it to the fibres. These fixatives thus show a strong affinity with both the fibres and the wood resin particles without causing aggregation of the particles.

The cPAMs (Fix D, FixE and Fix F) can be classified as “Colloid Disrupting” polymers but in some cases were found to be good fixatives and other cases poor. The high molar mass of the cPAMs is utilised for bridging particles and as a result they are used extensively as retention aids and for this reason they readily aggregate the wood resin particles to larger particle size which can interact with the fibres and also be entrapped in the fibre mat.

FixA (pDADMAC), FixB (pDADMAC) and FixH (p(AM-co-DADMAC)) maintain good fixation across the pH range studied,

but they are not good colloidal stabilisers. This would suggest that fixatives that contain pDADMAC are good fixatives. It is likely that this group of polymers also removes stabilising material (e.g. galactoglucomannans) from solution, in turn disrupting the colloidal stability of the wood extractive material left behind in the filtrate (i.e. white water).

Figure 11 depicts a conceptual model that shows the spectrum by which fixation of the wood resins can occur through either maintaining or disrupting colloidal wood resin stability. The two axes in Figure 11 represent the changes in colloidal stability and fixation that can occur. The upper section of the figure shows the situation in which the addition of polymer, such as guar gum, pDADMAC and pEI, may increase fixation of the pitch particles to the fibre surface while maintaining colloidal stability. Polymers which cause aggregation of the pitch (such as pAM) and also fixation would represent the situation in the lower right hand corner (aggregated pitch particles fixed to fibre). In some situations polymers may cause aggregation of the pitch particles but not fix the larger aggregates to the fibre surface (a change from the upper right hand corner to the lower right hand corner). Entrapment of the larger particles into the fibre mat may occur.

Factors such as pH and other additives may cause stabilisation or destabilisation of the pitch particles and cause the system to move up or down the y axis in Figure 11. The interaction and affinity between the polymer, wood resins and polymer which cause fixation will also be affected by the anionicity and surface area of the fibres and fines; the concentrations and distribution of the individual components of the wood extractives; the pH, temperature, counter ions, and stock consistency of the bulk solution. Variations in any of these factors in the papermaking process will cause the system to move along the x axis in Figure 11 and affect polymer performance and its ability to fix pitch.

CONCLUSIONS

From the papermakers perspective the higher molar mass pDADMAC, the p(AM-co-DADMAC) and guar gum were found to be the better fixatives across the pH range explored (4.75 pH – 8.06 pH). The performance of some of the polymers investigated was found to vary over the pH range investigated.

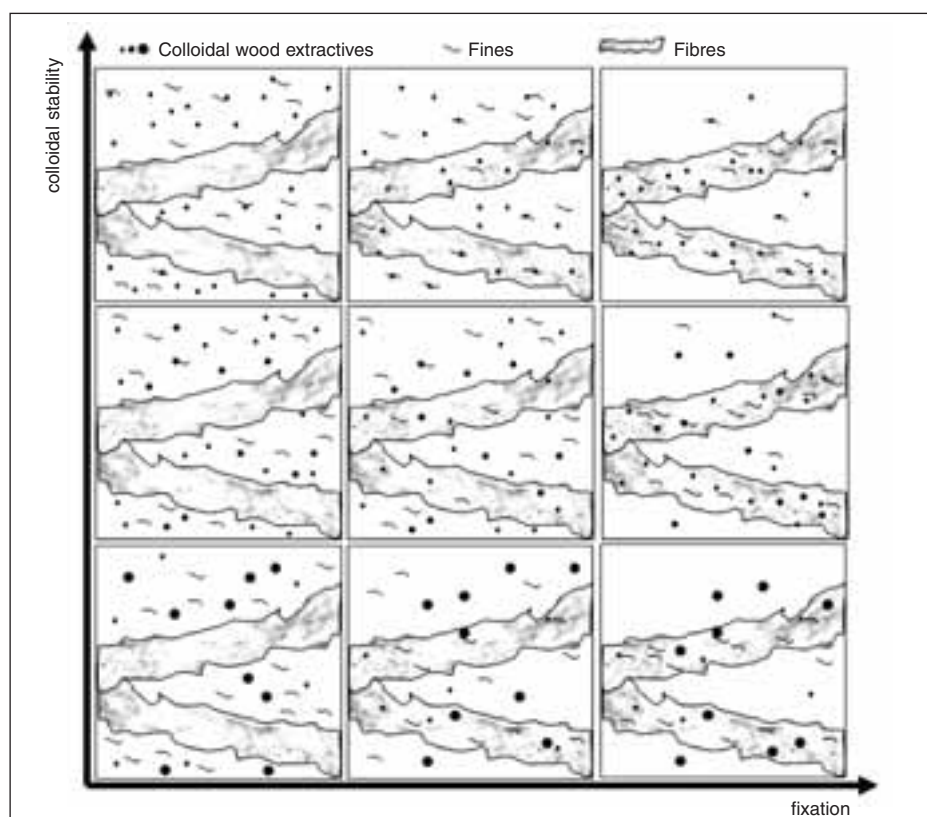


Fig. 11 Conceptual Model of fixation - Wood resin fixation versus colloidal wood resin stability.

Molar mass or cationic charge density alone does not predict polymer wood pitch fixation. The cationic polymers investigated can be categorised by how they affect the colloidal stability of the wood resin and their ability to attach the wood resins to the fibres. Disrupting colloidal stability can force the precipitation of colloidal wood extractive material onto the fibre and papermaking surfaces. It can also increase the colloidal particle size such that it becomes entrapped in the fibres and fibre mat. The cationic polymers that act as 'polymeric bridging' fixatives to improve fibre and filler retention, such as high molar mass pAM, achieve fixation through this mechanism of disrupting colloidal stability.

Guar gum and high MW pDADMAC were found to stabilise the colloids and also attach the colloids to the fibres. These polymers thus show a strong affinity to both the fibre surface and the wood resins without causing aggregation. The medium MW pDADMAC and p(AM-co-DADMAC) were found to maintain good fixation but were not necessarily good colloidal stabilisers.

ACKNOWLEDGEMENTS

This work was funded with industry support from Norske Skog Paper Mills (Australia) Pty. Ltd. and the Australian Research Council (ARC).

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Original manuscript received 18 May 2009, revision accepted 6 November 2009